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(54) **Planographic printing original plate and method of plate-making a planographic printing plate**

(57) A positive type planographic printing original plate which enables direct plate-making using a solid or semiconductor laser emitting infrared rays by recording an image from digital data of computers, is highly sensitive to an infrared laser and has stability to developing treatment, and a method of plate-making a positive type planographic printing plate which is resistant to occurrence of flaw inferences. The planographic printing original

plate includes a first layer which contains a polymer that is insoluble in water and soluble in alkaline water, and a second layer which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution containing an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in an alkali developing solution by action of one of light and heat. The layers are sequentially provided on a support.

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## Description

## BACKGROUND OF THE INVENTION

## 5 Field of the Invention

[0001] The present invention relates to a planographic printing original plate which has sensitivity in the infrared wavelength region and a method of plate-making a planographic printing plate using the planographic printing original plate, and particularly to a positive type planographic printing original plate that enables direct plate-making using an infrared laser controlled by digital signals of computers or the like and to a method of plate-making a planographic printing plate using the positive type planographic printing original plate.

## Description of the Related Art

15 [0002] Lasers have developed remarkably in recent years, and solid lasers and semiconductor lasers which respectively emit infrared rays in a wavelength range particularly from 760 nm to 1200 nm (occasionally referred to as an "infrared lasers" hereinafter), and which have high output power and are small-sized have come to be easily available. These infrared lasers are very useful as a recording light source for making a printing plate directly from digital data of computers or the like. Therefore, nowadays there are increased demand for image recording materials having high sensitivity to such an infrared recording light source, namely, image recording materials which are changed in solubility in a developing solution by irradiation with infrared rays.

20 [0003] Image forming materials having a photosensitive layer containing an acid generator and an acid-decomposable material as a positive type photosensitive layer which is solubilized by irradiation with activated light have been known. A photosensitive composition containing a compound having an orthocarboxylic or carboxylic acid amide acetal group is disclosed in the specification of U.S. Patent (USP) No. 3,779,779, a photosensitive composition containing a compound having an acetal or ketal group on its principal chain is disclosed in the publication of Japanese Patent Application Laid-Open (JP-A) No. 53-133429 (USP No. 4,247,611), and a composition containing a compound having a silyl ether group is disclosed in the publication of JP-A No. 60-37549.

25 [0004] However, these photosensitive compositions have sensitivity to ultraviolet rays and are solubilized in an alkali by exposure to ultraviolet rays to form a non-image portion and do not allow image exposure using infrared rays such as those of an inexpensive and compact semiconductor laser. In other words, infrared rays have a lower energy than ultraviolet rays, which are currently used as a light source for exposure, giving rise to the problem that it is hard to cause a photoreaction or the like, by which the solubility of an image recording material in a developing solution is changed, by exposure with infrared rays.

30 [0005] Meanwhile, as a technique enabling image exposure by infrared rays such as the rays of a semiconductor laser, a technique concerning an image forming material which has a photosensitive layer containing an acid generator, a resol resin, a novolac resin and an infrared radiation absorber and is used for the formation of a negative type image by performing heat treatment before developing treatment and after image exposure is disclosed in the specification of USP No. 5,340,699. These materials pose the problem that no positive image is formed if the aforementioned heat treatment is not performed and further has the disadvantage that sensitivity is low in both negative and positive types.

35 [0006] An image forming material having a photosensitive layer containing an acid generator, an acid-decomposable compound and an infrared radiation absorber has been disclosed in JP-A No. 9-171254 in recent years. In this system, the acid-decomposable compound is decomposed to form a positive type image by using, as a catalyst, an acid generated by irradiation with activated light. Therefore, a chemically large amplifying effect is obtained and the surface of the material irradiated with a laser has a high positive effect (developing is restrained in an unexposed portion and a restriction to developing is released or disappears in an exposed portion) resulting from light-heat conversion. However, heat generated in the vicinity of the surface reaches the deep portion of the material insufficiently. Hence there is a problem concerning heat diffusion in the vicinity of a support and only an insufficient effect is obtained in the deep portion when a support made of usual aluminum is used.

40 [0007] As a consequence, even if the image forming material is developed using an alkali, clear discrimination between an unexposed portion and an exposed portion is obtained with difficulty. Therefore a more improvement in sensitivity has been desired.

45 [0008] Also, there is a problem that a silicate contained in an alkali developing agent used when these image forming materials are developed after image exposure reacts with eluted components of the image forming material to form an insoluble material, which adheres to the surface of the image forming material whereby the surface of the image forming material is damaged when it is conveyed in a developing vessel.

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## SUMMARY OF THE INVENTION

[0009] An object of the present invention is to provide a positive type planographic printing original plate which enables direct plate-making using a solid laser or semiconductor laser emitting infrared rays by recording an image from digital data of computers or the like, which is highly sensitive to an infrared laser and which has high stability in developing treatment, and also to provide a method of plate-making a positive type planographic printing plate which is resistant to damage, the method being preferably applied to the planographic printing original plate.

[0010] The inventors of the present invention have focused their attentions on the layer structure of a positive type planographic printing original plate that enables direct plate-making by emitting infrared rays and on the characteristics of the surface layer and have made earnest studies. As a result, the inventors have found that the above problem can be solved by providing a thin layer which is not penetrative into an alkali developing solution and which is easily increased in solubility in an alkali developing solution by exposure with an infrared laser, on the surface of the planographic printing original plate, to complete the present invention.

[0011] Accordingly, the above object is attained by the following means. Specifically, a planographic printing original plate according to the present invention includes a first layer which contains a polymer that is insoluble in water and soluble in alkaline water and a second layer which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution that contains an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in the alkali developing solution by action of one of light and heat, which layers are sequentially provided on a support.

[0012] A method of plate-making a planographic printing plate according to the present invention includes: an exposure step of exposing an image onto a planographic printing original plate by an infrared laser, the planographic printing original plate being provided with a first layer which contains a polymer that is insoluble in water and soluble in alkaline water, and a second layer which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution that contains an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in the alkali developing solution by action of one of light and heat, which layers are sequentially provided on a support; and a developing step of removing an exposed portion of the second layer, which exposed portion has been increased in solubility in the alkali developing solution by image exposure, by the alkali developing solution which contains an organic compound having a buffering effect and a base as principal components, therewith dissolving and removing a portion of the first layer corresponding to a removed portion of the second layer by the alkali developing solution.

[0013] It is to be noted that, in the present invention, the polymer which is insoluble in water and soluble in alkaline water is, as the case may be, called simply "alkaline water-soluble polymer" as appropriate. Also, the expression "by action of one of light and heat" includes the meaning "by action of both light and heat".

[0014] In the method of plate-making a planographic printing plate of the present invention, it is considered that sensitivity to an infrared laser is bettered by disposing the second layer, which is an infrared-sensitive layer that is increased in solubility in an alkali developing solution by exposure, although the action is not clarified, on an exposing surface or in the vicinity thereof. Heat generated by exposure with the infrared laser is not diffused to the support and used efficiently to solubilize the first layer by disposing the first layer, which is made of the polymer, between the support and the infrared-sensitive layer to function as an insulating layer, thereby improving sensitivity. Also, in the unexposed portion, the second layer, which is not penetrative into the alkali developing solution, functions as a protective layer for the first layer, whereby developing stability is bettered and an image having high discrimination is formed.

[0015] In the method of plate-making a planographic printing plate according to the present invention, it is considered that the improved developing stability which characterizes the planographic printing original plate ensures that satisfactory developing can be carried out even if an alkali developing solution which contains an organic compound having a buffering effect and a base as principal components, and which contains no silicate is used, no insoluble material caused by the silicate is produced and plate-making resistant to flaw inclusions is allowed.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The planographic printing original plate of the present invention will be hereinafter explained in detail.

[0017] The planographic printing original plate according to the present invention comprises a first layer (hereinafter referred to as "alkaline water-soluble polymer layer" or simply as "polymer layer" as the case may be) which contains a polymer that is insoluble in water and soluble in alkaline water, and a second layer (hereinafter referred to as "infrared-sensitive layer" as the case may be), which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution containing an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in an alkali developing solution by action of one of light and heat, which layers are sequentially provided on a support.

[0018] These layers may be formed in this order and the planographic printing original plate may further comprise

known layers such as a surface layer, an intermediate layer and a backcoat layer insofar as the effect of the present invention is not impaired.

(First layer which contains a polymer that is insoluble in water and soluble in alkaline water <alkaline water-soluble polymer layer> )

[0019] In the present invention, the alkaline water-soluble polymer layer contains a polymer that is insoluble in water and soluble in alkaline water as its principal component. Because this polymer has excellent coatability, the polymer itself can form a layer.

[0020] The alkaline water-soluble polymer in the present invention includes homopolymers containing an acid group on the principal chain or side chain in a polymer, copolymers of these homopolymers and mixtures of these homopolymers and copolymers. Accordingly, the alkaline water-soluble polymer layer in the present invention is those having such characteristics as to dissolve when they are brought into contact with an alkali developing solution.

[0021] Among the aforementioned alkaline water-soluble polymers, those having an acid group given in each of the following (1) to (6) in view of solubility in an alkali developing solution.

- (1) Phenolic hydroxyl group (-Ar-OH)
- (2) Sulfonamide group (-SO<sub>2</sub>NH-R)
- (3) Substituted sulfonamide type acid group (hereinafter referred to as "activated imide group") (-SO<sub>2</sub>NHCOR, -SO<sub>2</sub>NHSO<sub>2</sub>R and -CONHSO<sub>2</sub>R)
- (4) Carboxylic acid group (-CO<sub>2</sub>H)
- (5) Sulfonic acid group (-SO<sub>3</sub>H)
- (6) Phosphoric acid group (-OPO<sub>3</sub>H<sub>2</sub>)

[0022] In the above (1) to (6), Ar represents a divalent aryl connecting group which may have a substituent and R represents a hydrocarbon group which may have a substituent.

[0023] Among alkaline water-soluble polymers having an acid group selected from the above (1) to (6), alkaline water-soluble polymers having (1) a phenol group, (2) a sulfonamide group and (3) an activated imide group are preferable and particularly alkaline water-soluble polymers having (1) a phenol group and (2) a sulfonamide group are most preferable to secure the solubility in an alkali developing solution and film strength sufficiently.

[0024] As the alkaline water-soluble polymer having an acid group selected from the above (1) to (6), the following compounds may be exemplified.

[0025] (1) Examples of the alkaline water-soluble polymer having a phenol group include novolac resins such as condensation polymers of phenol and formaldehyde, condensation polymers of m-cresol and formaldehyde, condensation polymers of p-cresol and formaldehyde, condensation polymers of an m-/p-cresol mixture and formaldehyde and condensation polymers of phenol, cresol (which may be m-, p- or m-/p- mixture types) and formaldehyde, condensation polymers of pyrogallol and acetone. Further, copolymers obtained by copolymerizing a compound having a phenol group on the side chain may be given as examples.

[0026] As examples of the compound having a phenol group, acrylamides, methacrylamides, acrylates, methacrylates or hydroxystyrenes which have a phenol group may be given.

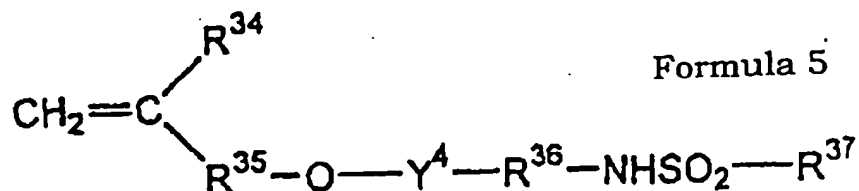
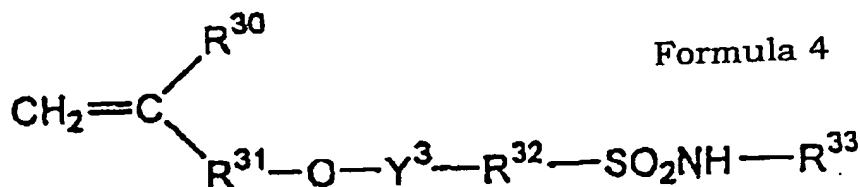
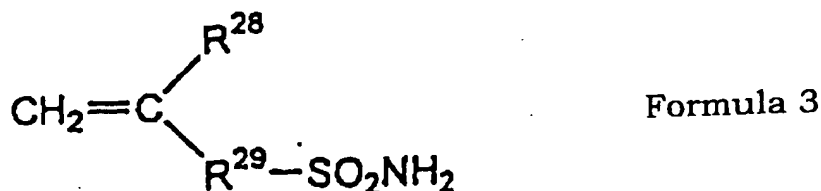
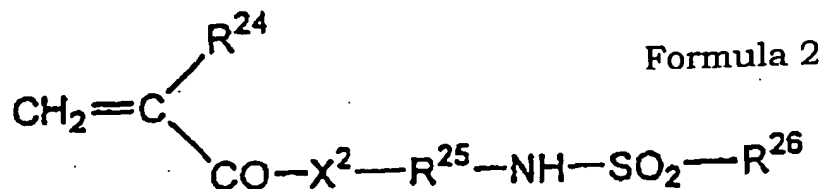
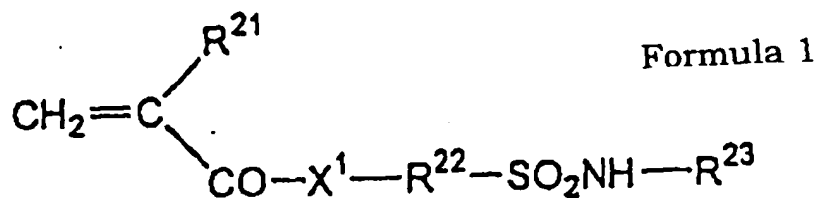
[0027] Specific examples of the compound having a phenol group include N-(2-hydroxyphenyl)acrylamide, N-(3-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)acrylamide, N-(2-hydroxyphenyl)methacrylamide, N-(3-hydroxyphenyl)methacrylamide, N-(4-hydroxyphenyl)methacrylamide, o-hydroxyphenylacrylate, m-hydroxyphenylacrylate, p-hydroxyphenylacrylate, o-hydroxyphenylmethacrylate, m-hydroxyphenylmethacrylate, p-hydroxyphenylmethacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, 2-(2-hydroxyphenyl)ethylacrylate, 2-(3-hydroxyphenyl)ethylacrylate, 2-(4-hydroxyphenyl)ethylacrylate, 2-(2-hydroxyphenyl)ethylmethacrylate, 2-(3-hydroxyphenyl)ethylmethacrylate and 2-(4-hydroxyphenyl)ethylmethacrylate.

[0028] These polymers may be used either singly or in combinations of two or more. In the case of combining these compounds, condensation polymers of a phenol containing an alkyl group having 3 to 8 carbon atoms as a substituent and formaldehyde such as condensation polymers of t-butylphenol and formaldehyde and condensation products of octylphenol and formaldehyde as described in the specification of USP No. 4,123,279 may be used together.

[0029] (2) As the alkaline water-soluble polymers having a sulfonamide group, polymers structured by a minimum structural unit, derived from a compound having a sulfonamide group, as its principal structural component may be exemplified.

[0030] Examples of the compound include compounds which contain one or more sulfonamide group in which at least one hydrogen atom is bonded to a nitrogen atom and one or more polymerizable unsaturated group in a molecule. Among these compounds, low molecular compounds having an acryloyl group, aryl group or vinyloxy group and a substituted or mono-substituted aminosulfonyl group or substituted sulfonylimino group in a molecule are preferable.

As examples, compounds represented by the following formulae 1 to 5 are given.



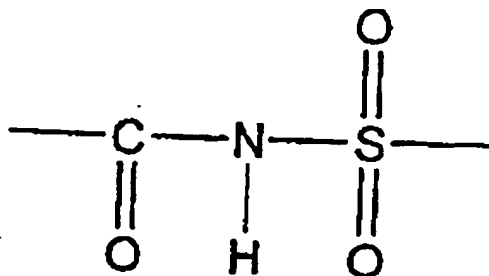
wherein  $\text{X}^1$  and  $\text{X}^2$  respectively represent -O- or -NR<sup>27</sup>-,  $\text{R}^{21}$  and  $\text{R}^{24}$  respectively represent a hydrogen atom or -CH<sub>3</sub>,  $\text{R}^{22}$ ,  $\text{R}^{25}$ ,  $\text{R}^{29}$ ,  $\text{R}^{32}$  and  $\text{R}^{36}$  respectively represent an alkylene, cycloalkylene, arylene or aralkylene group which has 1 to 12 carbon atoms and may have a substituent,  $\text{R}^{23}$ ,  $\text{R}^{27}$  and  $\text{R}^{33}$  respectively represent a hydrogen atom or an alkyl, cycloalkyl, aryl or aralkyl group which has 1 to 12 carbon atoms and may have a substituent,  $\text{R}^{26}$  and  $\text{R}^{37}$  respectively represent an alkyl, cycloalkyl, aryl or aralkyl group which has 1 to 12 carbon atoms and may have a substituent,  $\text{R}^{28}$ ,  $\text{R}^{30}$  and  $\text{R}^{34}$  respectively represent a hydrogen atom or -CH<sub>3</sub>,  $\text{R}^{31}$  and  $\text{R}^{35}$  respectively represent a single bond or an alkylene, cycloalkylene, arylene or aralkylene group which has 1 to 12 carbon atoms and may have a

substituent and  $Y^3$  and  $Y^4$  respectively represent a single bond or  $-CO-$ .

[0031] Among the compounds represented by the formulae 1 to 5, particularly m-aminosulfonylphenylmethacrylate, N-(p-aminosulfonylphenyl) methacrylamide, N-(p-aminosulfonylphenyl)acrylamide or the like may be preferably used in the planographic printing original plate of the present invention.

[0032] (3) As the alkaline water-soluble polymers having an activated imide group, polymers structured by a minimum structural unit, derived from a compound having an activated imide group, as its principal structural component may be exemplified.

[0033] Examples of the compound include compounds having one or more activated imide groups represented by the following structural



formula and one or more polymerizable unsaturated groups in a molecule.

[0034] Concretely, N-(p-toluenesulfonyl)methacrylamide or N-(p-toluenesulfonyl)acrylamide may be preferably used.

[0035] (4) As the alkaline water-soluble polymers having a carboxylic acid group, polymers whose principal structural component is a minimum structural unit derived from a compound having one or more carboxylic acid groups and one or more polymerizable unsaturated groups in a molecule may be exemplified.

[0036] (5) As the alkaline water-soluble polymers having a sulfonic acid group, polymers whose principal structural unit is a minimum structural unit derived from a compound having one or more sulfonic acid groups and one or more polymerizable unsaturated groups in a molecule may be exemplified.

[0037] (6) As the alkaline water-soluble polymers having a phosphoric acid group, polymers whose principal structural component is a minimum structural unit derived from a compound having one or more phosphoric acid groups and one or more polymerizable unsaturated groups in a molecule may be exemplified.

[0038] Among the aforementioned alkaline water-soluble polymers, particularly (1) alkaline water-soluble polymers having a phenolic hydroxyl group are preferred in the point that strong interaction can be obtained between each of these polymers and the aforementioned polyfunctional amine compound.

[0039] The minimum structural unit which constitutes the alkaline water-soluble polymer used for the positive type planographic printing original plate of the present invention and has an acid group selected from the above (1) to (6) is unnecessarily only one type in particular, but alkaline water-soluble polymers produced by copolymerizing two or more of these minimum structural units having the same or different acid groups may be used.

[0040] As the above copolymerization method, a conventionally known graft copolymerization method, block copolymerization method or random copolymerization method may be used.

[0041] As the aforementioned copolymer, those containing the compound which is to be copolymerized and has an acid group selected from the above (1) to (6) in an amount of 10 mol% or more are preferable and those containing the compound in an amount of 20 mol% or more are more preferable. When the amount of the compound is less than 10 mol%, there is a tendency that the development latitude can be improved insufficiently.

[0042] In the present invention, when the compound is copolymerized to form a copolymer, other compounds excluding an acid group of the above (1) to (6) may be used as the compound. Examples of these compounds excluding the acid group of the above (1) to (6) include compounds given by the following (m1) to (m12).

[0043] (m1) For example, acrylates or methacrylates, having an aliphatic hydroxyl group, such as 2-hydroxyethylacrylate and 2-hydroxyethylmethacrylate.

[0044] (m2) Alkylacrylates such as methylacrylate, ethylacrylate, propylacrylate, butylacrylate, amylacrylate, hexylacrylate, octylacrylate, benzylacrylate, 2-chloroethylacrylate, glycidylacrylate and N-dimethylaminoethylacrylate.

[0045] (m3) Alkylmethacrylates such as methylmethacrylate, ethylmethacrylate, propylmethacrylate, butylmethacrylate, amylmethacrylate, hexylmethacrylate, cyclohexylmethacrylate, benzylmethacrylate, 2-chloroethylmethacrylate, glycidylmethacrylate and N-dimethylaminoethylmethacrylate.

[0046] (m4) Acrylamides or methacrylamides such as acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide and N-ethyl-N-phenylacrylamide.

[0047] (m5) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether and phenyl vinyl ether.

[0048] (m6) Vinylesters such as vinyl acetate, vinylchloroacetate, vinyl butylate and vinyl benzoate.

[0049] (m7) Styrenes such as styrene,  $\alpha$ -methylstyrene, methylstyrene and chloromethylstyrene.

[0050] (m8) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone.

[0051] (m9) Olefins such as ethylene, propylene, isobutylene, butadiene and isoprene.

[0052] (m10) N-vinylpyrrolidone, N-vinylcarbazole, 4-vinylpyridine, acrylonitrile and methacrylonitrile.

[0053] (m11) Unsaturated imides such as maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide and N-(p-chlorobenzoyl)methacrylamide.

[0054] (m12) Unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid anhydride and itaconic acid.

[0055] As the alkaline water-soluble polymer used for the planographic printing original plate of the present invention, those, which may be homopolymers or copolymers, having a weight average molecular weight of 2,000 or more and a number average molecular weight of 500 or more are preferable in view of sensitivity and development latitude. Those having a weight average molecular weight in the range of 5,000 to 300,000 and a number average molecular weight in the range of 800 to 250,000 are more preferable. Also, those having a polydispersity index, which is the weight average molecular weight divided by the number average molecular weight, in the range of 1.1 to 10 are preferable.

[0056] When the copolymer is used in the present invention, copolymers in which the ratio by weight of the minimum structural unit derived from the compound which has an acid group that is selected from the above (1) to (6) and which constitutes the principal chain and/or side chain thereof, to the minimum structural unit excluding an acid group (1) to (6) which constitutes the principal chain and/or side chain thereof, is in a range from 50:50 to 5:95 are preferable and copolymers in which the above ratio is in a range from 40:60 to 10:90 are more preferable.

[0057] The aforementioned alkaline water-soluble polymers may be used either singly or in combinations of two or more.

[0058] Although the above alkaline water-soluble polymer may occupy 100% of the total solid of the material constituting an alkaline water-soluble polymer layer, it is used in an amount of preferably 30 to 99% by weight and more preferably 45 to 95% by weight because other components are used to improve layer formability and film characteristics.

[0059] When the amount of the above alkaline water-soluble polymer to be used is less than 30% by weight, there is a tendency that the layer formability and film characteristics of the polymer layer are deteriorated and hence such an excessively smaller amount is not preferable.

[0060] Examples of a solvent which can be used when the above alkaline water-soluble polymer to be used in the present invention is synthesized may include tetrahydrofuran, ethylene dichloride, cyclohexanone, methyl ethyl ketone, acetone, methanol, ethanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, diethylene glycol dimethyl ether, 1-methoxy-2-propanol, 1-methoxy-2-propyl acetate, N,N-dimethylformamide, N,N-dimethylacetamide, toluene, ethyl acetate, methyl lactate, ethyl lactate, dimethylsulfoxide and water. These solvents may be used either singly or in combinations of two or more.

[0061] The alkaline water-soluble polymer layer may further contain an infrared radiation absorber to improve sensitivity. As the infrared radiation absorber, the same compound as the infrared radiation absorbers which will be described in detail in the explanations of infrared-sensitive layers below.

[0062] A preferable amount of the infrared radiation absorber contained in the above alkaline water-soluble polymer layer is 0.01 to 50% by weight based on the total solid.

[0063] As materials constituting the above alkaline water-soluble polymer layer according to the present invention, besides the above materials, various additives may be used together according to the need.

[0064] For example, onium salts and thermally decomposable compounds such as aromatic sulfonates which are described as "Other components" which may be added to a positive type photosensitive composition in the publication of JP-A No. 11-174681 (USP No. 6,132,929), on and after paragraph 0067 are preferable to control the anti-dissolution ability of an image portion. Other than the above additives, additives such as cyclic acid anhydrides, phenols and organic acids those are useful to improve sensitivity, surfactants, print-out agents, and dyes and pigments as image colorants, which are described in the same publication as "Other additives" and may be likewise used in the present invention.

[0065] Moreover, for example, epoxy compounds, vinyl ether compounds, phenol compounds having a hydroxymethyl group as described in JP-A No. 8-276558 (USP No. 6,132,935) and crosslinkable compounds which are described in the publication of JP-A No. 11-160860 (E.P. Patent No. 919,868A1) and which have the ability to restrain alkali-dissolution may be added appropriately according to the object.

*(Second layer <infrared-sensitive layer> which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution that contains an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in the alkali developing solution by action of one of light and heat)*

5 [0066] The planographic printing original plate of the present invention comprises a second layer which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution containing an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in an alkali developing solution by the action of one of light and heat on the aforementioned alkaline water-soluble polymer formed on the support.

10 [0067] The above infrared-sensitive layer is preferably formed on the exposed surface of the outermost layer of the planographic printing original plate. In the exposed portion of the above infrared-sensitive layer, the aforementioned infrared radiation absorber generates heat by irradiation with an infrared laser. By the heat, the solubility of the binder forming the layer is increased whereas in the unexposed portion, the disability of penetrability into an alkali developing solution is maintained and only the exposed portion is solubilized to form a positive type image.

15 [0068] As the binder constituting the above infrared-sensitive layer, the alkaline water-soluble polymer which has been mentioned in detail for the above alkaline water-soluble polymer layer may be preferably used.

[0069] In the present invention, the infrared-sensitive layer functions as a film resistant to an alkali developing solution in the alkaline water-soluble polymer layer present between the support and the infrared-sensitive layer and it is therefore desirable to select polymers which are mutually insoluble as the alkaline water-soluble polymer used in the infrared-sensitive layer and in the alkaline water-soluble polymer layer respectively.

20 [0070] Here, the words "mutually insoluble" mean that a combination of two or more polymers (including the case where each is a copolymer or a phase of a mixture of two or more types) does not form one phase of a solid or liquid in appearance. This can be confirmed by a method in which the both are mixed and the section is observed visually or a photograph of the section is taken using a scanning type electron microscope and observed.

25 [0071] Examples of the polymers used in combination of two or more types of compounds which are mutually insoluble include urethane type polymer compounds, acrylic polymer compounds, styrene type polymer compounds, novolak resins, diazo resins, amide type polymer compounds and polyether compounds. These polymers can be made soluble in an alkali developing solution by introducing the above acid group into these polymers. Given as preferable examples of the combination of two or more polymers which are mutually insoluble are combinations of an acrylic or urethane type polymer compound and a novolac resin and a combination of a novolac resin and a diazo resin and a combination of an acrylic or a urethane type polymer compound and a diazo resin.

30 [0072] The aforementioned alkaline water-soluble polymers may be used either singly or in combinations of two or more and are used in an amount ranging from preferably 30 to 99% by weight and more preferably 40 to 95% by weight based on the total solid of the material constituting the infrared-sensitive layer in the planographic printing original plate of the present invention.

35 [0073] When the amount of the above alkaline water-soluble polymer to be used is less than 30% by weight, the durability of the infrared-sensitive layer tends to deteriorate whereas when the amount exceeds 99% by weight, the sensitivity and the durability tend to be lowered and the amounts out of the above range are not therefore preferable.

40 [0074] An infrared radiation absorber must be contained in the infrared-sensitive layer of the planographic printing original plate of the present invention in view of sensitivity. The infrared radiation absorber which may be used here is preferably used also for the above alkaline water-soluble polymer layer.

45 [0075] No particular limitation is imposed on the infrared radiation absorber which may be used in the present invention insofar as it has the ability of generating heat by irradiation with an infrared laser. It is however preferable to use an infrared radiation absorber having an onium salt type structure with the view of necessarily effecting a positive action (developing is restrained in an unexposed portion and a restriction to developing is released or disappears in an exposed portion whereby the exposed portion becomes soluble in an alkaline water) between structural units of polymers. Specifically, dyes such as a cyanine dye and pyrylium salt may be preferably used.

[0076] Preferable examples of the above dye include cyanine dyes described in the publication of each of JP-A No. 58-125246, JP-A No. 59-84356, JP-A No. 59-202829 and JP-A No. 60-78787 and cyanine dyes described in the specification of U.K. Patent No. 434,875.

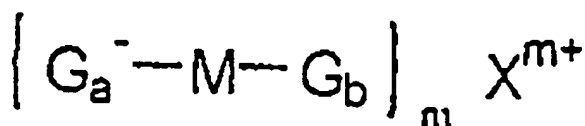
50 [0077] Near infrared absorption sensitizers described in the specification of USP No. 5,156,938 are preferably used. Further, substituted arylbenzo(thio)pyrylium salts described in the specification of USP No. 3,881,924, trimethine-thiopyrylium salts described in the publication of JP-A No. 57-142645 (USP No. 4,327,169), pyrylium compounds described in the publication of each of JP-A No. 58-181051, JP-A No. 58-220143, JP-A No. 59-41363, JP-A No. 59-84248, JP-A No. 59-84249, JP-A No. 59-146063 (USP No. 4,555,472) and JP-A No. 59-146061, cyanine dyes described in the publication of JP-A No. 59-216146 (USP No. 4,617,247), pentamethine-thiopyrylium salts described in the specification of USP No. 4,283,475 and the like and pyrylium compounds described in the publication of Japanese Patent Application Publication (JP-B) No. 5-13514 and JP-B No. 5-19702 (USP No. 4,663,260) are preferably used.



[0078] Near infrared absorbing dyes represented by the formulae (I) and (II) in the specification of USP No. 4,756,993 may also be given as preferable examples of the dye.

[0079] Moreover, anionic infrared radiation absorbers described in JP-A No. 11-338131 (E.P. Patent No. 945,264A) are also preferably used. The anionic infrared radiation absorbers indicate those in which the mother nucleus of a dye which substantially absorbs infrared rays is provided with no cationic structure but with an anionic structure.

[0080] Examples of these anionic infrared radiation absorbers include (c1) anionic metal complexes, (c2) anionic carbon black, (c3) anionic phthalocyanine and further (c4) compounds represented by the following formula 6. The counter cation of these anionic infrared radiation absorbers is a monovalent cation containing a proton or a polyvalent cation.



Formula 6

wherein  $G_a$  represents an anionic substituent,  $G_b$  represents a neutral substituent,  $X_{m+}$  represents a cation having one to  $m$  valences and containing a proton and  $m$  represents an integer from 1 to 6.

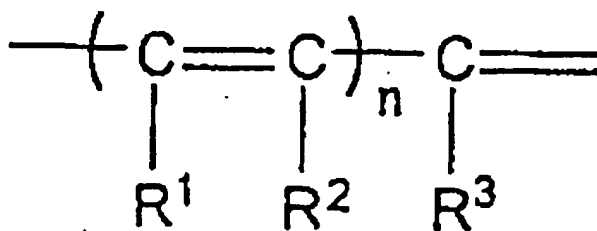
[0081] Here, the (c1) anionic metal complexes mean those in which a center metal in the complex portion which substantially absorbs light and a ligand exhibit an anionic nature as a whole.

[0082] Given as examples of the (c2) anionic carbon black are carbon black with which an anionic group such as a sulfonic acid, carboxylic acid or phosphonic acid group that is bonded as a substituent. In order to introduce each of these groups into carbon black, for example measures to oxidize carbon black using a predetermined acid may be taken as described in "Carbon Black Handbook" the third edition (edited by Carbon Black Association, April 5 in 1995, published by Carbon Black Association).

[0083] Anionic infrared radiation absorbers produced by ionically bonding an onium salt as a counter cation with an anionic group of the anionic carbon black are preferably used in the present invention. However, an adsorption material in which an onium salt is adsorbed to carbon black is excluded from these anionic infrared radiation absorbers which are preferably used in the present invention. Also, the effect of the present invention cannot be obtained by a simple adsorption material.

[0084] The (c3) anionic phthalocyanine is those in which an anionic group exemplified as the substituent in the previous explanation of (c2) is bonded to a phthalocyanine skeleton and exhibits an anionic nature as a whole.

[0085] Next, the compounds represented by the formula 6 of the above (c4) will be explained in detail. In the formula 6,  $M$  represents a conjugate chain, which may have a substituent or a cyclic structure. The conjugate chain  $M$  may be represented by the following formula.



wherein  $R^1$ ,  $R^2$  and  $R^3$  respectively represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group or an amino group wherein these groups may be combined to form a cyclic structure and  $n$  denotes an integer from 1 to 8.

[0086] Specific preferable examples of the anionic infrared radiation absorber represented by the above formula 6 are described in the specification of JP-A No. 11-338131 (E.P. Patents No. 945,264A), paragraphs 0094 to 0105.

[0087] Examples of the infrared radiation absorbers having an onium salt structure which are preferable examples of the infrared radiation absorber used in the present invention are those described as the specific examples (A-20 to A-75) in the specification of Japanese Patent Application No. 11-231399, paragraphs 0046 to 0061.

[0088] Each of these dyes which are infrared radiation absorbers may be added in the material constituting the infrared-sensitive layer in an amount of 0.01 to 50% by weight, preferably 0.1 to 10% by weight and particularly preferably 0.5 to 10% by weight based on the total solid. When the amount of the dye is less than 0.01% by weight, the sensitivity is reduced whereas when the amount exceeds 50% by weight, this will afford possibilities for the occurrence of contaminations in a non-image portion and generation of flaws during printing.

[0089] The material constituting the infrared-sensitive layer in the planographic printing original plate of the present invention may further contain other dyes and pigments for the purpose of improving sensitivity and development latitude.

[0090] As the other dye, commercially available dyes and known dyes described in literature, for example, "Dye Handbook" (edited by Organic Synthetic Chemical Association, issued in 1970) may be used. Specific examples of these dyes include azo dyes, azo dyes of metal complex salts, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, diimmonium dyes, aminium dyes, squarylium dyes and metal thiolate complexes.

[0091] As the other pigments, commercially available pigments and pigments described in "Color Index (C.I.) Handbook, "The Newest Pigment Handbook" (edited by Japan Pigment Technical Association, published in 1977), "The newest Pigment Applied Technology" (CMC Shuppan, published in 1986) and "Printing Ink Technology" (CMC Shuppan, published in 1984) may be utilized.

[0092] Given as examples of the type of pigment which can be used are black pigments, yellow pigments, orange pigments, brown pigments, red pigments, violet pigments, blue pigments, green pigments, fluorescent pigments, metal powder pigments, other pigments and polymer bond dyes. Specifically, insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine type pigments, anthraquinone type pigments, perylene and perinone type pigments, thioindigo type pigments, quinacridone type pigments, dioxazine type pigments, isoin-dolinone type pigments, quinophthalone type pigments, dying lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments and carbon black may be used. Among these pigments, carbon black is preferable.

[0093] These pigments may be used without being surface-treated or after they are surface-treated. As the method of surface treatment, a method of coating the surface with a resin or wax, a method of sticking a surfactant and a method of bonding a reactive material (e.g., a silane coupling agent, epoxy compound and polyisocyanate) to the surface of a pigment are considered. The aforementioned methods for surface treatment are described in "Qualities and Application of Metal Soap" (Saiwai Shobo), "Printing Ink Technology" (CMC Shuppan, published in 1984) and "The newest Pigment Applied Technology" (CMC Shuppan, published in 1986).

[0094] The particle diameter of the above pigment is in a range from preferably 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ , more preferably 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$  and particularly preferably 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ . When the particle diameter of the pigment is less than 0.01  $\mu\text{m}$ , this is not preferable in view of the stability of the dispersion in the coating solution for the image infrared-sensitive layer. On the other hand, when the particle diameter exceeds 10  $\mu\text{m}$ , this is not preferable in view of the uniformity of the formed layer.

[0095] As a method of dispersing the above pigment, known dispersion techniques used for the production of ink or a toner may be used. As examples of dispersing machines, a ultrasonic dispersion machine, sand mill, attritor, pearl mill, super mill, ball mill, impeller, disperser, KD mill, colloid mill, dynatron, three-roll mill and pressure kneader may be given. The details of these dispersing machines are described in "The newest Pigment Applied Technology" (CMC Shuppan, published in 1986).

[0096] The amount of the above pigment to be added is 0.01 to 50% by weight and more preferably 0.1 to 10% by weight based on the total solid of the material constituting the infrared-sensitive layer. When the amount of the pigment is less than 0.01% by weight, only an insufficient effect of improving sensitivity is obtained whereas when the amount exceeds 50% by weight, there is a fear of the occurrence of contaminations to a non-image portion and reduced durability of the layer.

[0097] Among the aforementioned dyes and pigments, those which absorb infrared rays or near infrared rays are particularly preferable. Also, the dyes and pigments may be used in combinations of two or more.

[0098] Various additives may be added to the material constituting the infrared-sensitive layer in the planographic printing original plate of the present invention.

[0099] For example, a polyfunctional amine compound may be contained. This polyfunctional amine compound has the ability (crosslinking ability) to stabilize the film structure of the infrared-sensitive layer by allowing the polyfunctional amine compound to coexist with the aforementioned alkaline water-soluble polymer because the amine compound interacts strongly with an alkali-soluble group contained in the polymer. Such a polyfunctional amine compound means amine compounds having at least two more functional groups. If the number of functional groups is one, no crosslinking effect is produced and hence no addition effect is obtained. The lower limit of the number of functional groups is preferably 3 or more in view of the formability of a more strong network. The upper limit of the number of functional groups is preferably 10 or less and more preferably 6 or less in view of adaptability to production and in order not to form an insoluble complex caused by strong interaction between polyfunctional groups.

[0100] The polyfunctional amine compound as an additive is preferably soluble or dispersible in water. If the polyfunctional amine compound has water-solubility or water-dispersibility sufficient in the so-called neutral water, a developing solution penetrates rapidly into the inside of the infrared-sensitive layer to remove the infrared-sensitive layer and the polymer layer is thereby brought into contact with the developing solution and the alkaline water-soluble polymer constituting the polymer layer is dissolved in a developing solution and removed when alkali developing explained later is performed, bringing about high developing ability without impairing the discrimination of an image. In the present invention, it is preferable that the amine compound be dissolved in water in an amount of 0.5 g/l or more to exhibit the "water-soluble" ability and be dispersed in water in an amount of 0.5 g/l or more to exhibit the "water-dispersing" ability.

[0101] It is not preferable that the above polyfunctional amine compound used in the present invention have an onium structure in view of developing ability. As examples of the polyfunctional compound used preferably in the present invention, compounds obtained by adding an amine compound to a commercially available polyfunctional polymerizable monomer are given.

[0102] The aforementioned polyfunctional amine compounds used in the present invention may be used either singly or by mixing two or more.

[0103] When the above polyfunctional amine compound is added to the infrared-sensitive layer in the present invention, the amount to be added is in a range between preferably 3% by weight and 50% by weight and more preferably 10 and 20% by weight based on the above alkaline water-soluble polymer. When the amount is less than 3% by weight, the effect of the present invention is insufficiently produced and therefore such an amount out of the above range is not preferable. On the other hand, when the amount exceeds 50% by weight, the adaptability to application and the coatability are lowered and therefore such an amount out of the above range is not preferable.

[0104] Also, for example, other onium salts, aromatic sulfonic compounds and aromatic sulfonate compounds function as thermally decomposable materials. Therefore, if these materials are added, the ability to restrain the dissolution of an image portion can be improved. So the addition of these materials is preferable.

[0105] As the above onium salt, diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts and arsonium salts may be given. Preferable examples of the onium salt used in the present invention include diazonium salts described in the publication of JP-A No. 5-158230 (USP No. 5,370,965), ammonium salts described in the specification of each of USP No. 4,069,055 and USP No. 4,069,056 or in the publication of JP-A No. 3-140140, phosphonium salts described in the specification of USP No. 4,069,055 or USP No. 4,069,056, iodonium salts described in E.P. Patent No. 104,143, the specification of each of USP No. 339,049 and No. 410,201 and the publication of JP-A No. 2-150848 or JP-A No. 2-296514, sulfonium salts described in the specification of each of E.P. Patents No. 370,693, No. 233,567, No. 297,443 and No. 297,442, USP No. 4,933,377, USP No. 3,902,114, USP No. 410,201, USP No. 339,049, USP No. 4,760,013, USP No. 4,734,444 and USP No. 2,833,827, D.T. Patents No. 2,904,626, No. 3,604,580 and No. 3,604,581, selenonium salts described in J.V. Crivello et al, Macromolecules, 10 (6), 1307 (1977) or J.V. Crivello et al, J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979) and arsonium salts described in C.S. Wen et al, Teh, Proc. Conf. Rad. Curing ASIA, p478 Tokyo, Oct (1988).

[0106] As the counter ion of the above onium salt, hexafluorophosphoric acid and alkyl aromatic sulfonic acids such as triisopropylphenylsulfonic acid and 2,5-dimethylbenzenesulfonic acid may be given as examples although a usual one may be used.

[0107] The amount of the above onium salt is preferably 1 to 50% by weight, preferably 5 to 30% by weight and particularly preferably 10 to 30% by weight based on the total solid content of the material constituting the infrared-sensitive layer of the planographic printing original plate.

[0108] Also, dyes having large absorption in the visible region may be used as a colorant for an image. Given as specific examples of these dyes are Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS and Oil Black T-505 (the above products are manufactured by Orient Chemical Industries), Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000), Methylene blue (CI52015), Aizen Spiron Blue C-RH (manufactured by Hologaya Chemical) and dyes described in the publication of JP-A No. 62-293247.

[0109] The addition of these dyes ensures that discrimination between an image portion and a non-image portion after an image is formed is made clear and is hence preferable. The amount to be added is preferably in a range from 0.01 to 10% by weight based on the total solid content of the material constituting the infrared-sensitive layer in the planographic printing original plate.

[0110] Also, cyclic anhydrides, phenols and organic acids may be added for the purpose of further improving sensitivity. As the cyclic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxo- $\Delta$  4-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride,  $\alpha$ -phenylmaleic anhydride, succinic anhydride, pyromellitic dianhydride or the like may be used.

[0111] Given as examples of the above phenols are bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4"-trihydroxytriphenylmethane and 4,4',3",4"-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane.

[0112] Examples of the aforementioned organic acids include sulfonic acids, sulfinic acids, alkyl sulfates, phosphonic acids, phosphates and carboxylic acids as described in the publication of each of JP-A No. 60-88942 and JP-A No. 2-96755, specifically p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethyl sulfate, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluylic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid and ascorbic acid.

[0113] The proportion occupied by the above cyclic acid anhydride, phenols and organic acids in the total solid of the material constituting the infrared-sensitive layer of the planographic printing original plate is preferably 0.05 to 20% by weight, more preferably 0.1 to 15% by weight and particularly preferably 0.1 to 10% by weight.

[0114] In the material constituting the infrared-sensitive layer in the planographic printing original plate of the present invention, nonionic surfactants as described in the publication of each of JP-A No. 62-251740 and JP-A No. 3-208514 and amphoteric surfactants as described in the publication of each of JP-A No. 59-121044 and JP-A No. 4-13149 may be added to improve process stability to developing conditions.

[0115] Specific examples of the above nonionic surfactant include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearic acid monoglyceride and polyoxyethylene nonylphenyl ether.

[0116] Specific examples of the above amphoteric surfactant include alkyl di(aminoethyl)glycine, alkyl polyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazoliniumbetaine and N-tetradecyl-N,N-betaine types (e.g., Amorgen K (trademark), manufactured by Daiichi Kogyo).

[0117] The proportion occupied by the nonionic surfactant and the amphoteric surfactant in the total solid of the material constituting the infrared-sensitive layer of the planographic printing original plate is preferably 0.05 to 15% by weight and more preferably 0.1 to 5% by weight.

[0118] In the material constituting the infrared-sensitive layer of the planographic printing original plate, a print-out agent for obtaining a visible image just after heating by exposure and dyes and pigments as image colorants may be added.

[0119] As typical examples of the above print-out agent, a combination of a compound (photosensitive acid generator) which releases an acid by heat caused by exposure and an organic dye capable of forming a salt may be given. Specific examples of these combinations may include a combination of an o-naphthoquinonediazido-4-sulfonic acid halogenide and an organic dye which can form a salt as described in the publication of each of JP-A No. 50-36209 and JP-A No. 53-8128 and a combination of a trihalomethyl compound and an organic dye which can form a salt as described in the publication of each of JP-A No. 53-36223, JP-A No. 54-74728, JP-A No. 60-3626, JP-A No. 61-143748, JP-A No. 61-151644 and JP-A No. 63-58440.

[0120] Given as examples of the above trihalomethyl compound are an oxazole type compound and triazine type compound, which both have high stability with time and provide a clear print-out image.

[0121] Also, the addition of an epoxy compound, a vinyl ether compound, a phenol compound having a hydroxymethyl group or an alkoxymethyl group as described in the publication of JP-A No. 8-276558 and a crosslinkable compound having alkali dissolution-restraining ability as described in the publication of JP-A No. 11-160860 is desirable in view of storage stability.

[0122] Moreover, in the material constituting the infrared-sensitive layer, a plasticizer is added as required to provide a film with flexibility. For example, butylphthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate or oligomers or polymers of acrylic acid or methacrylic acid is preferably used.

[0123] Also, a surfactant for bettering coatability, for example, a fluorine type surfactant as described in the publication of JP-A No. 62-170950 may be added. The amount of the surfactant is preferably 0.01 to 1% by weight and more preferably 0.05 to 0.5% by weight based on the total amount of the infrared-sensitive layer.

#### *(Method of plate-making a planographic printing plate)*

[0124] Using the planographic printing original plate of the present invention, a positive type planographic printing plate may be produced according to the following plate-making method.

[0125] The planographic printing plate is produced by dissolving the material constituting the alkaline water-soluble polymer layer of the planographic printing original plate of the present invention comprising the aforementioned each component in a solvent, applying the resulting solution to an appropriate support, thereafter dissolving the material constituting the infrared-sensitive layer in a solvent and applying the resulting solution to the above alkaline water-soluble polymer layer.

[0126] Examples of the solvent to be used here include, though not limited to, ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane,  $\gamma$ -butyrolactone, toluene

and water.

[0127] These solvents are used singly or by mixing two or more. The concentration of the above components (total solid content including additives) is preferably 1 to 50% by weight.

[0128] The amount (solid content) of the alkaline water-soluble polymer layer formed on the support and obtained after it is applied and dried is preferably 0.1 to 5.0 g/m<sup>2</sup> in general in the case where the printing plate is used as a photosensitive printing plate, though it differs depending on the use. Also, the amount of the infrared-sensitive layer to be applied is preferably 0.1 to 3.0 g/m<sup>2</sup> taking the film strength into consideration, though the infrared-sensitive layer is preferably thin as far as it has the ability to protect the above alkaline water-soluble polymer layer from a developing solution.

[0129] As an application method, various methods may be used. Examples of these methods may include bar coater coating, rotary coating, spray coating, curtain coating, dip coating, air knife coating, blade coating and roll coating.

[0130] Example of the above support may include dimensionally stable plate materials such as paper, paper on which plastics (e.g., a polyethylene, polypropylene and polystyrene) are laminated, metal plates (e.g., aluminum, zinc or copper), plastic films (e.g., cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate and polyvinylacetal) and paper or plastic films on which a metal such as aluminum, zinc or copper is deposited or laminated.

[0131] As the above support used in the present invention, polyester films or aluminum plates are preferable. Among these materials, aluminum plates which are dimensionally highly stable and relatively inexpensive are particularly preferable.

[0132] A preferable aluminum plate is a pure aluminum plate and an alloy plate containing aluminum as its principal component and other minute elements or may be a plastic film on which aluminum is laminated or deposited.

[0133] These different elements contained in the aluminum alloy include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. The amount of the other elements in the aluminum alloy is 10% by weight or less.

[0134] Although particularly preferable aluminum in the present invention is pure aluminum, aluminum containing other minute elements is acceptable since the production of perfectly pure aluminum is difficult from the viewpoint of refining technologies. The composition of the aluminum plate used in the present invention is not specified in this manner and an aluminum plate which is a conventionally known and common material may be optionally utilized.

[0135] The thickness of the aluminum plate to be used in the present invention is about 0.1 mm to 0.6 mm, preferably 0.15 mm to 0.4 mm and particularly preferably 0.2 mm to 0.3 mm.

[0136] The aluminum plate is roughened and used. Degreasing treatment using, for example, a surfactant, organic solvent or aqueous alkaline solution is carried out as desired to remove rolling oil left on the surface prior to roughening of the surface of the aluminum plate.

[0137] The treatment for roughening the surface of the aluminum plate is performed using various methods, for example, a method in which the surface is mechanically roughened, a method in which the surface is roughened by dissolving the surface electrochemically and a method in which the surface is selectively dissolved chemically.

[0138] As the above mechanical method, a known method such as a ball polishing method, brush polishing method, blast polishing method or buff polishing method may be used. As the electrochemical surface roughing method, there is a method in which roughing treatment is carried out in a hydrochloric acid or nitric acid electrolyte by using a.c. or d.c. current. Also, a method of a combination of the both may be utilized as disclosed in JP-A No. 54-63902.

[0139] The aluminum plate roughened in this manner is subjected to anodic oxidation treatment as desired to improve the water-retentivity and wear resistance of the surface after it is subjected to alkali etching treatment and neutralizing treatment according to the need.

[0140] As an electrolyte to be used for the anodic oxidation treatment of the aluminum plate, various electrolytes which form a porous oxide film can be used. Sulfuric acid, phosphoric acid, oxalic acid or chromic acid or a mixed acid of these acids is used as the electrolyte in general. The concentration of each of these electrolytes is properly determined according to the type of electrolyte.

[0141] Although treating conditions for anodic oxidation cannot be specified as a whole because they vary depending on the type of electrolyte to be used, a proper range of each condition are as follows in general: the concentration of an electrolyte in a solution: 1 to 80% by weight, solution temperature: 5 to 70 °C, current density: 5 to 60 A/dm<sup>2</sup>, voltage: 1 to 100 V, electrolytic time: 10 seconds to 5 minutes.

[0142] If the amount of the anodic oxidation film is smaller than 1.0 g/m<sup>2</sup>, only insufficient printing durability is obtained. Also, a non-image portion of the planographic printing plate is easily damaged and the so-called "flaw stain", namely, a phenomenon that ink is stuck to a flaw portion during printing tends to occur.

[0143] The surface of aluminum is subjected to hydrophilic treatment according to the need after it is subjected to the anodic oxidation treatment. As the hydrophilic treatment usable in the present invention, there is a method using an alkali metal silicate (e.g., an aqueous sodium silicate) as disclosed in the specification of each of USP No. 2,714,066,

USP No. 3,181,461, USP No. 3,280,734 and USP No. 3,902,734. In this method, the support is subjected to dipping treatment or electrolytic treatment using an aqueous sodium silicate solution.

[0144] In addition to this method, a method of treating using fluorinated potassium zirconate as disclosed in the publication of JP-B No. 36-22063 and a method of treating using polyvinylphosphonic acid as disclosed in the specification of each of USP No. 3,276,868, USP No. 4,153,461 and USP No. 4,689,272 are used.

[0145] In the planographic printing original plate, an undercoat layer may be formed as required between the above support and the above alkaline water-soluble polymer layer.

[0146] As the component for the undercoat layer, a variety of organic compounds are used. The organic compound is selected from carboxymethyl cellulose, dextrin, gum arabic, phosphonic acids having an amino group such as 2-aminoethylphosphonic acid, organic phosphonic acids such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid which may have a substituent, organic phosphoric acids such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid which may have a substituent, organic phosphinic acid such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid which may have a substituent, amino acids such as glycine and  $\beta$ -alanine and hydrochlorides of an amine having a hydroxyl group such as a hydrochloride of triethanolamine. These acids may be used by mixing two or more.

[0147] Also, the aforementioned polyfunctional amine compounds may be added to the undercoat layer as previously mentioned. In this case, the undercoat layer may be formed either using the polyfunctional amine compound together with the aforementioned organic compound or using only the polyfunctional amine compound.

[0148] The above undercoat layer may be formed by the following method.

[0149] Specifically, there are a method in which a solution obtained by dissolving the above organic compound and/or the polyfunctional amine compound in water or an organic solvent such as methanol, ethanol and methyl ethyl ketone or a mixture of these solvent is applied to the aluminum plate and dried to form an undercoat layer and a method in which the aluminum plate is soaked in a solution obtained by dissolving the above organic compound and/or the polyfunctional amine compound in water or an organic solvent such as methanol, ethanol or methyl ethyl ketone or a mixed solvent of these solvents to allow these compounds to adsorb to the aluminum plate, followed by washing with water or the like and drying to form an undercoat layer.

[0150] In the former method, the solution containing the organic compound and/or the polyfunctional amine compound in a concentration of 0.005 to 10% by weight may be applied using various methods.

[0151] In the latter method, the concentration of the solution is 0.01 to 20% by weight and preferably 0.05 to 5% by weight, soaking temperature is 20 to 90 °C and preferably 25 to 50 °C, soaking time is 0.1 second to 20 minutes and preferably 2 second to 1 minute. As examples of the solution used for this, basic materials such as ammonia, triethylamine and potassium hydroxide and acidic materials such as hydrochloric acid and phosphoric acid are given. Each of these solutions is used to adjust a pH ranging from 1 to 12. A yellow dye may also be added to improve the reproducibility of the tone of the planographic printing original plate.

[0152] The amount of the undercoat layer is appropriately 2 to 200 mg/m<sup>2</sup> and preferably 5 to 100 mg/m<sup>2</sup>. When the above amount to be applied is less than 2 mg/m<sup>2</sup>, only insufficient printing durability can be obtained whereas when the amount exceeds 200 mg/m<sup>2</sup>, the same result is also obtained.

[0153] The produced planographic printing plate is usually subjected to image exposure and developing treatment to form an image. As a light source for activated rays used in the image exposure, a light source which emits in a wavelength range from the near infrared region to the infrared region and a solid laser and a semiconductor laser are particularly preferable.

[0154] As a developing solution and replenishing solution used in the developing of the planographic printing original plate of the present invention, a conventionally known alkali developing solution containing, as its principal components, an organic compound having a buffering effect and a base and substantially excluding silicon dioxide is used. In this invention, such a developing solution is hereinafter referred to as "non-silicate developing solution". Here, the word "substantially" means that the presence of unavoidable impurities and minute silicon dioxide as a byproduct is tolerated.

[0155] In a step of developing the planographic printing original plate of the present invention, the effect of restraining the occurrence of flaws is improved by applying the above non-silicate developing solution. As the aqueous alkali solution, those having a pH of 12.5 to 13.5 are preferable.

[0156] The "non-silicate developing solution" used in the plate-making the planographic printing plate of the present invention contains an organic compound having a buffering effect and a base as its principal components as aforementioned. Given as examples of the organic compound having a buffering effect are saccharides (particularly those represented by the formula (I) and (II)) described in the publication of JP-A No. 8-220775 as compounds having a buffering effect, oximes (particularly those represented by the formula (III)), phenols (particularly those represented by the formula (IV)) and fluorinated alcohols (particularly those represented by the formula (V)).

[0157] Among compounds represented by the formulae (I) to (V), preferable compounds are saccharides represented by the formula (I) or (II) and phenols represented by the formula (V) and more preferable compounds are non-reducing

[0163] An alkali agent as a base may be appropriately selected from conventionally known alkali agents and combined with the above organic compound having a buffering effect.

[0164] Examples of the above alkali agent include inorganic alkali agents such as sodium hydroxide, potassium hydroxide, lithium hydroxide, trisodium phosphate, tripotassium phosphate, triammonium phosphate, disodium phosphate, dipotassium phosphate, diammonium phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate and ammonium borate, potassium citrate, tripotassium citrate and sodium citrate.

[0165] Also, organic alkali agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, trisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine and pyridine may be given as preferable examples of the alkali agent.

[0166] These alkali agents are used singly or in combinations of two or more.

[0167] Among the above alkali agents, sodium hydroxide and potassium hydroxide are preferable. This is because the pH can be controlled in a wide pH range by controlling the amount of the alkali agent to be added to the non-reducing sugar.

[0168] Also, trisodium phosphate, tripotassium phosphate, sodium carbonate and potassium carbonate are preferable since each itself has a buffering effect.

[0169] Further, it is known that when developing using an automatic developing machine, a large number of planographic printing plates can be treated without exchanging the developing solution in a developing tank for a long period of time by adding an aqueous solution (hereinafter referred to as "replenishing solution" as the case may be) having a higher alkalinity than the developing solution. In the present invention, this replenishing system is preferably used.

[0170] Various surfactants and organic solvents may be added as required to the aforementioned developing solution and replenishing solution with the intention of achieving the promotion of or restriction on developing and improving the dispersion of developing residues and the affinity of the printing graphic image portion to ink. Given as preferable examples of the surfactant are anionic, cationic, nonionic and amphoteric surfactants.

[0171] Further, hydroquinone, resorcinol and reducing agents such as sodium or potassium salts of inorganic acids such as sulfurous acid or sulfurous acid hydroacid and further organic carboxylic acid, antifoaming agents and water softeners may be added.

[0172] The planographic printing plate developed using the aforementioned developing solution and replenishing solution is aftertreated using washing water, a rinse solution containing a surfactant and the like and a desensitizing solution containing gum arabic or a starch derivative. These treatments are used variously by combining them as aftertreatment when a printing plate which is made according to the above method using the planographic printing original plate of the present invention.

[0173] In plate-making and printing fields in recent years, an automatic developing machine for printing plates has been widely used for rationalization and standardization of plate-making works. The planographic printing plate obtained in the present invention may be treated in this automatic developing machine. This automatic developing machine usually consists of a developing section and an aftertreatment section, comprising a system for conveying a printing plate, respective process solution vessels and a spray system. In the developing machine, each process solution is drawn by a pump is sprayed from a spray nozzle while an exposed printing plate is carried horizontally to carry out developing. Also, a method is known today in which a printing plate is dipped and conveyed in a process solution vessel filled with a process solution by using, for example, a submerged guide roll. In such an automatic process, the printing plate may be treated while a replenishing solution is supplied to each process solution corresponding to a

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sugars such as saccharose or sulfosalicylic acid among the saccharides represented by the formula (I) or (II). The non-reducing sugars include trehalose type oligosaccharides in which reducing groups are bonded among them, glycosides in which a reducing group of sugars is bonded with non-saccharides and sugar-alcohols obtained by adding hydrogen to reduce sugars.

[0158] Examples of the above trehalose type oligosaccharide include saccharose and trehalose and examples of the above glycosides include alkyl glycosides and phenol glycosides and mustard oil glycosides.

[0159] Examples of the above sugar-alcohols include D,L-arabitol, ribitol, xylitol, D,L-sorbitol, D,L-anethol, D,L-iditol, D,L-talitol, dulcitol and allodulcitol.

[0160] Moreover, maltitol obtained by hydrogenating a disaccharide and reductants (reduced starch syrup) obtained by hydrogenating an oligosaccharide may be given as preferable examples.

[0161] Among the above non-reducing sugars, sugar-alcohols and saccharose are preferred and particularly D-sorbitol, saccharose and reduced starch syrup are more preferable because these sugars have a buffering effect in a proper pH range.

[0162] The aforementioned organic compounds having a buffering effect may be used either singly or in combinations of two or more. The proportion occupied by the sugar in a developing solution is preferably 0.1 to 30% by weight and more preferably 1 to 20% by weight.

throughput and operating time. Also, the so-called nonreturnable treating system using a substantially unused process solution to carry out treatment can be applied.

[0174] If unnecessary image portions (e.g., a film edge mark of an original image film) are present on the planographic printing plate after image exposure, developing, washing with water and/or rinsing and/or gum-drawing are carried out, measures may be taken to erase the unnecessary image portions.

[0175] As the above erasing method, a method in which an erasing liquid is applied to the unnecessary image portion and is allowed to stand as it is for a fixed time, followed by washing with water as described in the publication of JP-B No. 2-13293 is preferred. However, a method in which activated light rays guided by an optical fiber are applied to the unnecessary image portion, followed by developing as described in the publication of JP-A No. 59-174842 may also be utilized.

[0176] The planographic printing plate provided with the above treatments may be subjected to a printing step after a desensitizing gum is applied as desired to the printing plate. Burning treatment may be performed with the intention of more improving the printing durability. When the planographic printing plate is treated by burning, it is preferable to treat the planographic printing plate by using a surface regulating solution prior to the burning as described in the publication of each of JP-B No. 61-2518, JP-B No. 55-28062, JP-A No. 62-31859 and JP-A No. 61-159655. As the treating method, a method in which the surface regulating solution is applied to the surface of the planographic printing plate by using sponge or absorbent cotton impregnated with the solution, a method in which the planographic printing plate is immersed in a butt filled with the surface regulating solution to apply the solution to the planographic printing plate and a method of applying using an automatic coater may be used. Also, it is more preferable to make the applied amount uniform by a squeegee or a squeegee roller after the application is finished. The amount of the surface regulating solution to be applied is appropriately 0.03 to 0.8 g/m<sup>2</sup> (dry weight).

[0177] The planographic printing plate coated with the surface regulating solution is dried and then heated to high temperatures by using a burning processor (e.g., Burning Processor: BP-1300) placed on the market by Fuji Photo Film. Heating temperature and time in this case are preferably in a range from 180 to 300 °C and in a range from 1 to 20 minutes respectively though these conditions differ depending upon the type of component forming an image.

[0178] The planographic printing plate which has been treated by burning may be subjected appropriately to treatments which are conventionally performed such as washing and gum-drawing according to the need. In the case where a surface regulating solution containing an aqueous polymer compound and the like is used, the so-called desensitizing treatment such as gum-drawing can be omitted.

[0179] The planographic printing plate obtained by the aforementioned treatments is incorporated into an offset printer and used to print sheets.

#### EXAMPLES

[0180] The present invention will be hereinafter explained in detail by way of examples, which, however, are not intended to be limiting of the present invention.

#### *(Synthesis of a specific copolymer)*

##### *Synthetic Example <specific copolymer 1>*

[0181] A 500 ml three-neck flask equipped with a stirrer, a condenser tube and a dropping funnel was charged with 31.0 g (0.36 mol) of methacrylic acid, 39.1 g (0.36 mol) of ethyl chloroformate and 200 ml of acetonitrile and the mixture was stirred under cooling in an ice-water bath. To the mixture was added dropwise 36.4 g (0.36 mol) of triethylamine by using the dropping funnel over one hour. After the addition was completed, the ice-water bath was dismantled and the mixture was stirred at ambient temperature for 30 minutes.

[0182] To the reaction mixture was added 51.7 g (0.30 mol) of p-aminobenzenesulfonamide and the mixture was stirred for one hour under heating at 70 °C in an oil bath. After the reaction was finished, the mixture was poured into 1 l of water while stirring water and the resulting mixture was stirred for 30 minutes. The mixture was treated by filtration to take out the precipitate, which was then made into a slurry by adding 500 ml of water. The slurry was subjected to filtration and the resulting solid was dried to obtain N-(p-aminosulfonylphenyl)methacrylamide as a white solid (yield: 46.9 g).

[0183] Next, a 20 ml three-neck flask equipped with a stirrer, a condenser tube and a dropping funnel was charged with 4.61 g (0.0192 mol) of N-(p-aminosulfonylphenyl)methacrylamide, 2.94 g (0.0258 mol) of ethylmethacrylate, 0.80 g (0.015 mol) of acrylonitrile and 20 g of N,N-dimethylacetamide and the mixture was stirred under heating at 65 °C in a hot water bath. 0.15 g of "V-65" (manufactured by Wako Pure Chemical Industries) was added to the mixture, which was then stirred for 2 hours in a nitrogen stream while the temperature was kept at 65 °C. To the reaction mixture were further added dropwise 4.61 g of N-(p-aminosulfonylphenyl)methacrylamide, 2.94 g of ethylmethacrylate, 0.80 g



of acrylonitrile and 0.15 g of a mixture of N,N-dimethylacetamide and "V-65" over 2 hours by using the dropping funnel. After the addition was completed, the resulting mixture was further stirred at 65 °C for 2 hours. After the reaction was finished, 40 g of methanol was added to the mixture, followed by cooling. The resulting mixture was poured into 2 l of water while water was stirred. The mixture was stirred for 30 minutes and then the precipitate was taken out by filtration, followed by drying to obtain 15 g of a white solid.

[0184] The weight average molecular weight (polystyrene standard) of this specific copolymer 1 was measured by gel permeation chromatography. As a result, the weight average molecular weight was 53,000.

*(Manufacturing of a substrate)*

[0185] A 0.3-mm-thick aluminum plate (Material 1050) was washed with trichloroethylene to degrease. Then the surface of the aluminum plate was grained using a nylon brush and a 400 mesh pumice/water suspension and was then thoroughly washed with water. This plate was immersed in an aqueous 25% sodium hydroxide solution at 45 °C for 9 seconds to carry out etching, followed by washing. The plate was further immersed in 20% nitric acid for 20 seconds and then washed. At this time, the amount of etching on the grained surface was about 3 g/m<sup>2</sup>. Next, the plate was formed with a 3 g/m<sup>2</sup> d.c. anodic oxidation film by using 7% sulfuric acid as the electrolyte at a current density of 15 A/dm<sup>2</sup>. After that, the plate was washed with water and dried. Further, the following undercoat solution 1 was applied to the plate and then the film was dried at 90 °C for one minute. The amount of the dried coat was 10 mg/m<sup>2</sup>.

*<Undercoat solution 1>*

[0186]

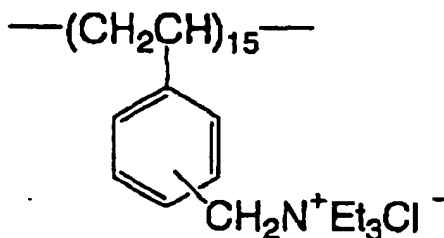
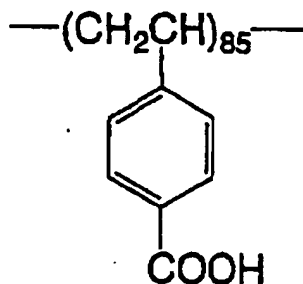
- β-alanine      0.5 g
- Methanol      95 g
- Water        5 g

[0187] Moreover, the resulting plate was treated in an aqueous solution of 2.5% by weight of sodium silicate at 30 °C for 10 seconds. The following undercoat solution 2 was applied to the plate and the film was dried at 80 °C for 15 seconds to obtain a substrate. The amount of the dried coat was 15 mg/m<sup>2</sup>.

*<Undercoat solution 2>*

[0188]

- Compound described below      0.3 g
- Methanol      100 g
- Water        1 g



Molecular weight 28000

(Example 1)

(Formation of a first layer (alkaline water-soluble polymer layer))

- 5 [0189] The following photosensitive solution 1-A was prepared. The photosensitive solution 1-A was applied to the resulting substrate such that the applied amount was 0.3 g/m<sup>2</sup> to form a first layer.

<Photosensitive solution 1-A>

10 [0190]

- Specific copolymer 1 0.75 g
- Fluorine type surfactant 0.05 g

15 (Megafac F-177; Dainippon Ink and Chemicals)

[0191]

- $\gamma$ -butyrolactone 10 g
- 20 • Methyl ethyl ketone 10 g
- 1-methoxy-2-propanol 1 g

(Formation of a second layer (infrared-sensitive layer))

- 25 [0192] The following photosensitive solution 1-B was prepared. The photosensitive solution 1-B described below was applied to the first layer such that the applied amount was 1.5 g/m<sup>2</sup> to form a second layer.

<Photosensitive solution 1-B>

30 [0193]

- m, p-Cresol novolac (ratio of m to p = 6/4, weight average molecular weight: 3,500, 0.5% by weight of unreacted cresol was contained) 1.00 g
- p-toluenesulfonic acid 0.003 g
- 35 • Tetrahydrophthalic anhydride 0.03 g
- Cyanine dye A (following structure) 0.017 g
- Dye in which the counter ion of Victoria Pure Blue BOH is made to be 1-naphthalenesulfonic acid anion 0.015 g
- Fluorine type surfactant 0.05 g

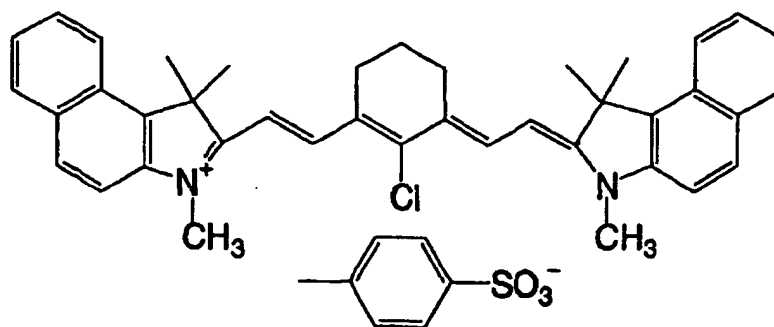
40 (Megafac F-177; Dainippon Ink and Chemicals)

[0194]

- $\gamma$ -butyrolactone 10 g
- 45 • Methyl ethyl ketone 10 g
- 1-methoxy-2-propanol 1 g

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Cyanine dye A

[0195] The resulting planographic printing plate was exposed at a main scanning speed of 5 m/sec by using a semiconductor laser having an output power of 500 mW, a wavelength of 830 nm and a beam diameter of 17  $\mu\text{m}$  ( $1/e^2$ ). The plate was then developed using a PS processor 900 VR manufactured by Fuji Photo Film which processor was provided with two types of developing solution (developing solutions 1 and 2) which had the following compositions (including no silicate) and differ in dilution and a rinse solution FR-3 (diluted at a ratio of 1:7).

[0196] At this time, exposure values required to form an image by each developing solution and a difference (development latitude) between these exposure values was recorded. Also, 60 planographic printing plates (30 cm x 65 cm) were treated using the developing solution 1 and thereafter the image portion of the treated plate was observed to confirm the presence or absence of flaws which were considered to be caused by insoluble substances in the developing solution visually. These results are shown in Table 1.

<Developing solution 1>

[0197]

- D-sorbitol 5.1 parts by weight
- Sodium hydroxide 1.1 parts by weight
- Triethanolamine/ethylene oxide adduct (30 mol) 0.03 parts by weight
- Water 93.9 parts by weight

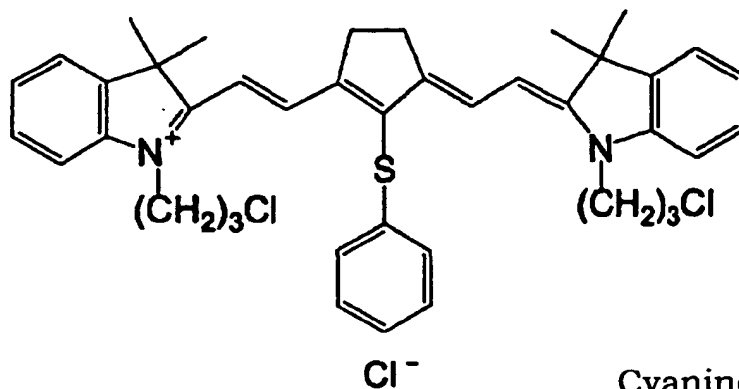
<Developing solution 2>

[0198]

- D-sorbitol 5.1 parts by weight
- Sodium hydroxide 1.1 parts by weight
- Triethanolamine/ethylene oxide adduct (30 mol) 0.03 parts by weight
- Water 140.7 parts by weight

(Example 2)

[0199] A planographic printing plate was produced as Example 2 in the same manner as in Example 1 except that the cyanine dye A used for the photosensitive solution 1-B in Example 1 was replaced by a cyanine dye B. The planographic printing plate of Example 2 was evaluated in the same manner as in Example 1. The results are shown in Table 1 below.



(Example 3)

[0200] A planographic printing plate was produced as Example 3 in the same manner as in Example 1 except that the cyanine dye A used for the photosensitive solution 1-B in Example 1 was replaced by carbon black (Printex L6, manufactured by Degussa). The planographic printing plate of Example 3 was evaluated in the same manner as in Example 1. The results are shown in Table 1 below.

(Comparative Example 1)

[0201] A planographic printing plate was produced in the same manner as in Example 1 except that the cyanine dye A used for the photosensitive solution 1-B in Example 1 was not used and was evaluated in the same manner as in Example 1. The results are shown in Table 1 below.

Table 1

	Infrared radiation absorber	Sensitivity (mJ/cm <sup>2</sup> )		Development latitude	Flaws in image portions
		Developing solution 1	Developing solution 2		
Example 1	Cyanine dye A	120	125	5	None
Example 2	Cyanine dye B	130	140	10	None
Example 3	Carbon black	135	140	5	None
Comparative example 1	None	No image was formed			
Comparative example 2	Cyanine dye A	115	120	5	Present

(Comparative Example 2)

[0202] The same planographic printing plate as in Example 1 was manufactured and exposed in the same manner as in Example 1. The plate was then developed using a PS processor 900 VR manufactured by Fuji Photo Film which processor was provided with a developing solution DP-4 (including a silicate) manufactured by Fuji Photo Film and a rinse solution FR-3 (diluted at a ratio of 1:7). At this time, as DP-4, the following two types differing in the level of dilution were prepared: one type (called a developing solution 1) diluted at a ratio of 1:8 and another type (called a developing solution 2) diluted at a ratio of 1:12. Exposure values required to form an image by each developing solution and a difference (development latitude) between these exposure values was recorded. Also, 60 planographic printing plates (30 cm×65 cm) were treated using the developing solution 1 (diluted at a ratio of 1:8) and thereafter the image portion of the treated plate was observed to visually confirm the presence or absence of flaws which were considered to be

caused by insoluble substances in the developing solution. These results are shown in Table 1.

[0203] As is clear from Table 1, the planographic printing plate obtained by carrying out plate-making according to the method of the present invention by using the planographic printing original plate of the present invention was superior in sensitivity and development latitude and no flaw was observed in an image portion. On the other hand, the planographic printing original plate of Comparative Example 1 containing no infrared radiation absorber in the infrared-sensitive layer formed no image. Also, the planographic printing original plate of Comparative Example 2 which was treated for plate-making by using an alkali developing solution containing a silicate had flaws generated in its image portion.

[0204] The present invention ensures that plate-making can be attained directly from digital data of computers or the like using a solid laser or semiconductor laser emitting infrared rays and a positive type planographic printing original plate which has high sensitivity to the above infrared laser and high stability to developing treatment and a method of the plate-making a positive type planographic printing plate which method is preferably applied to the planographic printing original plate and resistant to the occurrence of flaw inferiorities can be obtained.

## Claims

### 1. A planographic printing original plate comprising:

a first layer which contains a polymer that is insoluble in water and soluble in alkaline water; and a second layer which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution that contains an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in the alkali developing solution by action of one of light and heat;

which layers are sequentially provided on a support.

2. A planographic printing original plate according to claim 1, wherein the polymer that is insoluble in water and soluble in alkaline water contained in said first layer has at least one acidic group selected from the group consisting of (1) a phenolic hydroxyl group, (2) a sulfonamide group, (3) a substituted sulfonamide type acid group, (4) a carboxylic acid group, (5) a sulfonic acid group and (6) a phosphoric acid group at at least one of a principal chain and a side chain.

3. A planographic printing original plate according to claim 1 or 2, wherein the polymer that is insoluble in water and soluble in alkaline water contained in said first layer has a weight average molecular weight in the range of 5,000 to 300,000, has a number average molecular weight in the range of 800 to 250,000, and has a polydispersity index, which is the weight average molecular weight divided by the number average molecular weight, in the range of 1.1 to 10.

4. A planographic printing original plate according to any of claims 1 through 3, wherein the binder contained in said second layer contains a polymer which is insoluble in water and soluble in alkaline water and which is incompatible with the polymer in said first layer that is insoluble in water and soluble in alkaline water.

5. A planographic printing original plate according to any of claims 1 through 4, wherein a combination of the polymer which is insoluble in water and soluble in alkaline water and which is contained in said first layer, and a polymer which is insoluble in water and soluble in alkaline water and which is contained in the binder of said second layer, is a combination selected from the group consisting of an acrylic polymer compound and a novolac resin, an acrylic polymer compound and a diazo resin, a urethane type polymer compound and a novolac resin, a urethane type polymer compound and a diazo resin, and a novolac resin and a diazo resin.

### 6. A method of plate-making a planographic printing plate, the method comprising:

an exposure step of exposing an image onto a planographic printing original plate by an infrared laser, the planographic printing original plate being provided with a first layer which contains a polymer that is insoluble in water and soluble in alkaline water, and a second layer which contains an infrared radiation absorber and a binder, which is not penetrative into an alkali developing solution that contains an organic compound having a buffering effect and a base as principal components, and which is increased in solubility in the alkali developing solution by action of one of light and heat, which layers are sequentially provided on a support; and a developing step of removing an exposed portion of the second layer, which exposed portion has been in-

creased in solubility in the alkali developing solution by image exposure, by the alkali developing solution which contains an organic compound having a buffering effect and a base as principal components, therewith dissolving and removing a portion of the first layer corresponding to a removed portion of the second layer by the alkali developing solution.

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7. The method according to claim 6, wherein the organic compound having the buffering effect is a compound selected from the group consisting of saccharides, oximes, phenols and fluorinated alcohols.

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